

## Electronic Supplementary Information for A Band-Gap-Graded CZTSSe Solar Cell with 12.3 % Efficiency

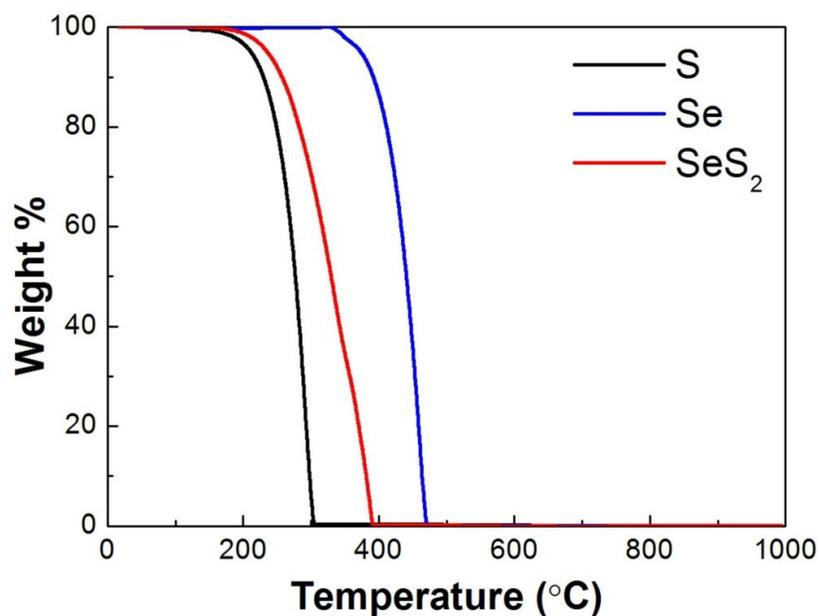
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**Fig. S1** TGA data for the S, Se, and SeS<sub>2</sub> sources.

Fig. S1 shows the thermogravimetric analysis (TGA) results of the S, Se, and SeS<sub>2</sub> sources obtained using a thermal analyzer (Q2000, TA Instruments). S and Se show the lowest and highest thermal vaporization temperatures, respectively, because of their characteristic physical properties. The temperatures at 50% weight loss ( $T_{50}$ ) of the S, Se, and SeS<sub>2</sub> samples are 230 °C, 440 °C, and 330 °C, respectively. The thermal vaporization temperature of the mixture chemical SeS<sub>2</sub> is between those of S and Se. In addition, the declination of the TGA curve of SeS<sub>2</sub> is less steep than those of S and Se, indicating that the vaporization behavior of SeS<sub>2</sub> is

moderate compared with those of S and Se. The thermal vaporization of  $\text{SeS}_2$  proceeds at temperatures ranging from 190 to 400 °C, whereas pure S and Se show rapid thermal vaporization from 130 to 300 °C and 340 to 470 °C, respectively. Based on these results, the thermal vaporization of  $\text{SeS}_2$  is less rapid than that of pure S or pure Se, and therefore, appropriate control of the chalcogenization reaction might be possible if the hybrid chalcogen source  $\text{SeS}_2$  is used in the chalcogenization process.

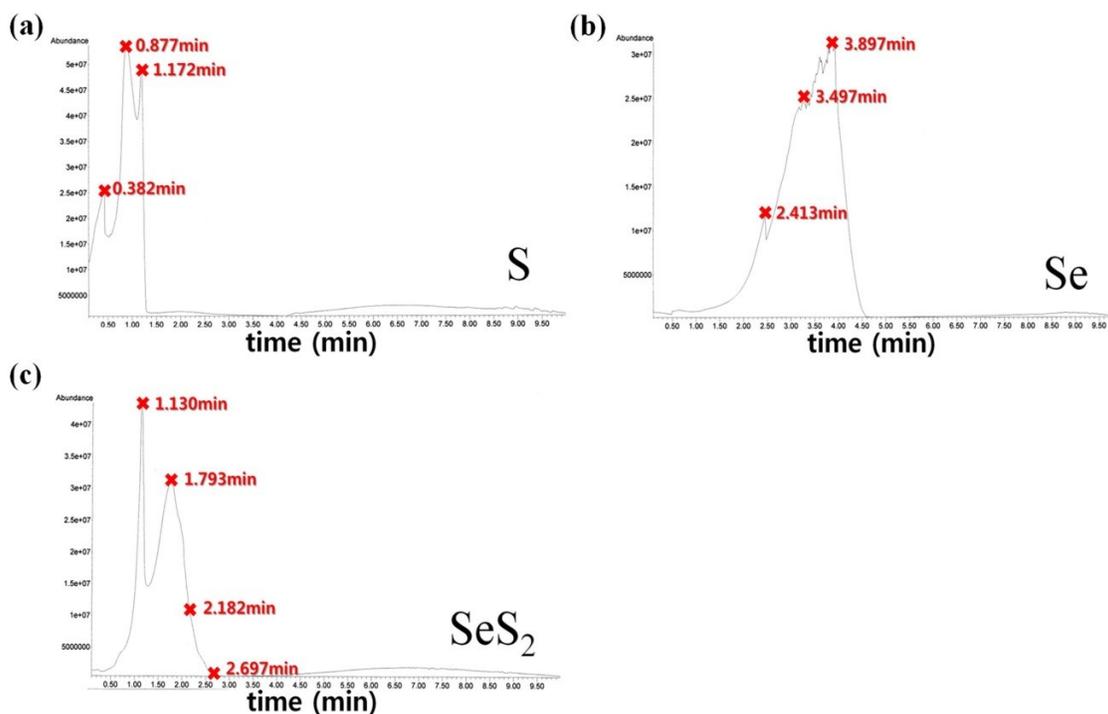
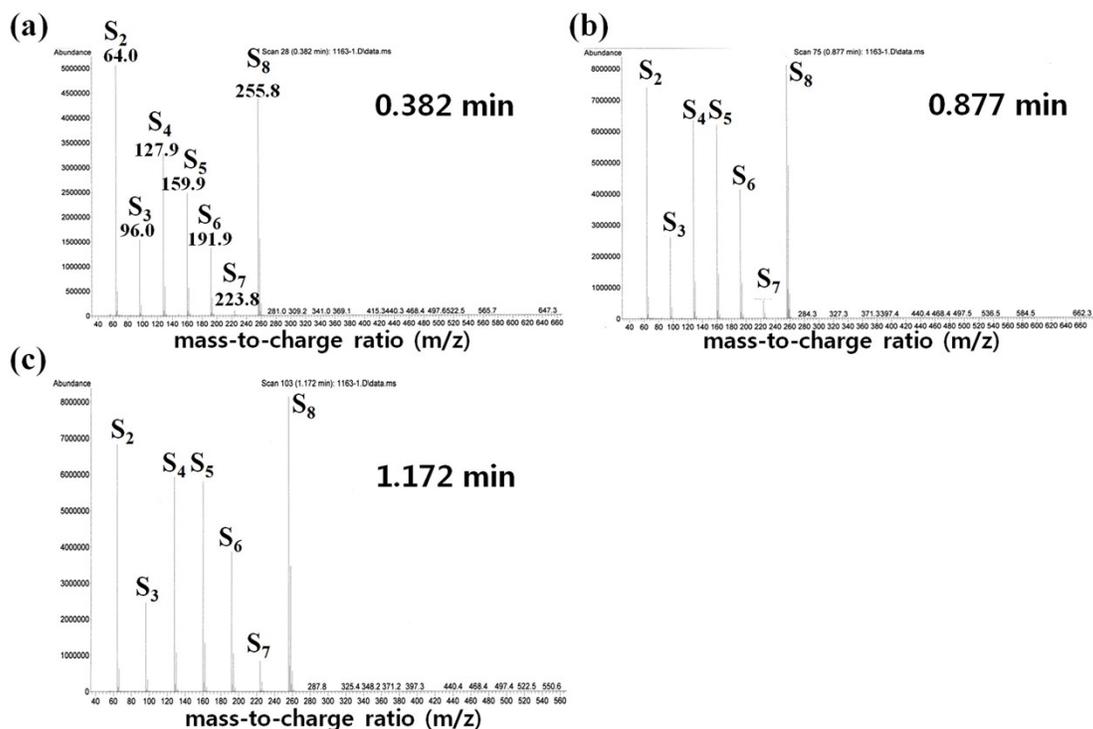
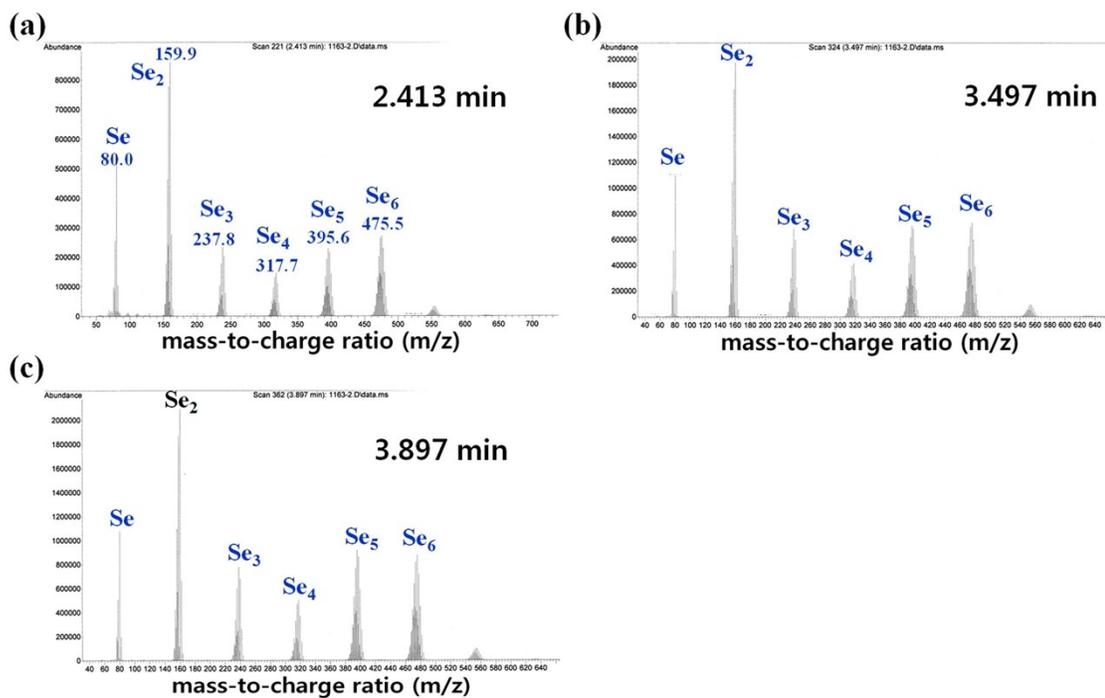


Fig. S2 Mass spectra of the S, Se, and  $\text{SeS}_2$  sources.

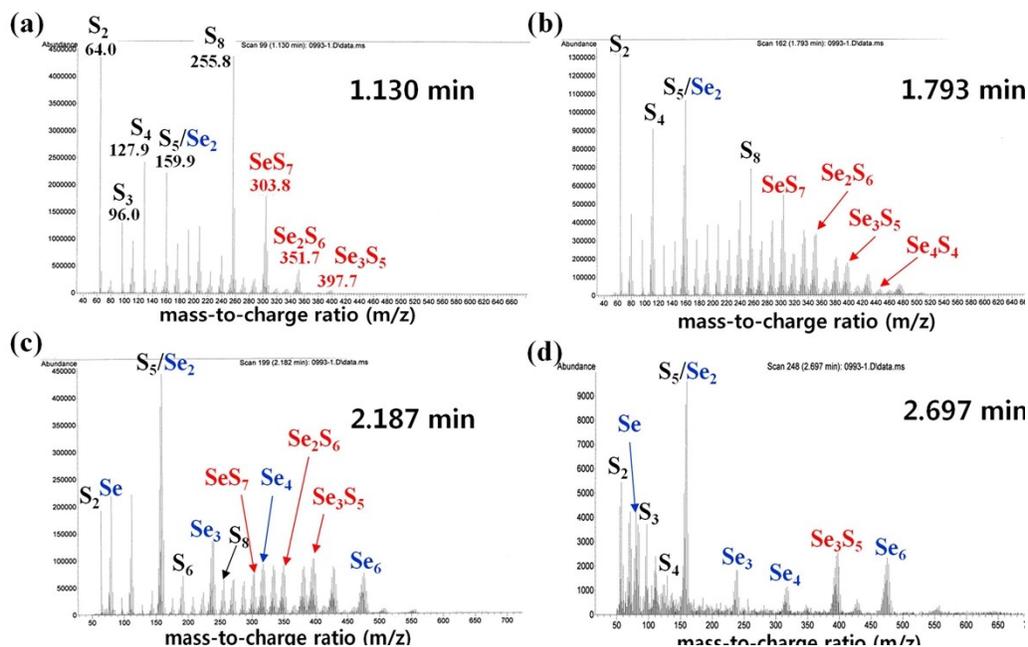
To verify which species are vaporized over time, the mass spectrum of each chalcogen source was measured using a gas chromatograph mass spectrometer (7890A 5975C DIP/MS, Agilent) at 300 °C. Fig. S2 shows the mass spectroscopy results of the three chalcogen chemicals. Although pure S and Se each show a single group of mass peaks, SeS<sub>2</sub> shows two different groups of mass peaks. A sharp mass peak at an early time is correlated with elemental S, and a subsequent broad peak may be attributable to Se<sub>x</sub>S<sub>8-x</sub>. To identify the types of thermally vaporized elements, mass spectra based on the mass-to-charge ratio (m/z) of each chalcogen chemical at different times were acquired.



**Fig. S3** Mass spectra of the S source at different times: (a) 0.382 min, (b) 0.877 min, and (c) 1.172 min.



**Fig. S4** Mass spectra of the Se source at different times: (a) 2.413 min, (b) 3.497 min, and (c) 3.897 min.



**Fig. S5** Mass spectra of the  $\text{SeS}_2$  source at different times: (a) 1.130 min, (b) 1.793 min, (c) 2.182 min, and (d) 2.697 min.

Fig. S3 shows the mass spectra of S at different times, and Fig. S4 shows the mass spectra of Se at different times. For both S and Se, the mass spectra show the same peak positions with respect to  $m/z$ , regardless of the time, and the peak positions exactly correspond to multiples of the atomic weights of S and Se, respectively. Thus, the products of the thermal vaporization of pure S and Se remain the same throughout the thermal treatment procedure. However, one chalcogen source,  $\text{SeS}_2$ , shows different mass spectra than S and Se (Fig. S5). First, as the measurement time increases, the mass spectrum of  $\text{SeS}_2$  shows different peak positions and intensities. Therefore, the products of thermal vaporization of  $\text{SeS}_2$  vary with respect to the thermal treatment conditions. In the early period, most of the peaks of the mass spectrum resemble those of pure S. As the measurement time increases, strong new peaks, which do not resemble those of S or Se, grow. Calculating the atomic weights of  $\text{Se}_x\text{S}_{8-x}$  revealed that these new peaks are in agreement with the products of the thermal vaporization of  $\text{SeS}_2$ . From this result, we could suppose that  $\text{SeS}_2$  has a strong chemical bond between the S and Se atoms, and therefore,  $\text{SeS}_2$  produces a mixture,  $\text{Se}_x\text{S}_{8-x}$ , via thermal heating. As the measurement time approaches the end of the mass spectrum, most of the mass peaks are the same as those of Se and  $\text{Se}_x\text{S}_{8-x}$ . Based on this analysis of the mass spectra of  $\text{SeS}_2$ , we can explain the thermal

vaporization of  $\text{SeS}_2$  as being composed of three stages: In the first stage, S is released. In the second stage,  $\text{Se}_x\text{S}_{8-x}$  mixtures are released. Finally, in the third stage, Se is released. This stepwise thermal vaporization of the chalcogen chemical  $\text{SeS}_2$  is very effective at controlling the chalcogenization reaction of CZTSSe precursor thin films.